Preparation of Anion Exchange Membrane by Amination of Chlorinated Polypropylene and Ethylenediamine and its Properties

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ABSTRACT: An anion exchange membrane was prepared by amination of chlorinated polypropylene (CPP) and ethylenediamine (EDA) at a low temperature and was investigated with respect to not only its physical properties but also its electrochemical properties. The degrees of amination were 46.05, 47.07, 50.56, and 56.58% at 30, 40, 50, and 55°, respectively. The CPP membrane had no water uptake, whereas, that of the CPP-EDA membrane was 0.153, 0.243, 0.309, and 0.410 g of H_2O/g of dry membrane, respectively, with increasing amination. The CPP-EDA membranes possessed an ion exchange capacity in the range 0.557–1.498 mequiv/g of dry membrane and a fixed ion concentration in the range 4.198–5.114 mequiv/g of H_2O. The ionic conductivity of the CPP-EDA membrane was highest when the water uptake was highest. Those of the CPP-EDA membrane were in the range 0.475×10^{-2}–0.999×10^{-2} S/cm. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2296–2301, 2010

Key words: crosslinking; films; ion exchangers; membranes; swelling

INTRODUCTION

The development of synthetic ion exchange membrane, reported by Juda in 1949,[1] and Juda and McRae in 1950,[2] stimulated both commercial and academic interest in such membranes and the related process.[3] Ion exchange membranes have now been commercially used in processes such as electrodialysis and diffusion dialysis for concentration or deionizing aqueous electrolyte solutions.[3,4] Recently, there has been growing interest in developing anion exchange membranes to replace caustic alkaline electrolyte solution for alkaline fuel cells.[5–7]

The anion exchange membranes are primarily prepared from polymers with functional amine groups.

Amination is considered as one of the most important ways of functionalize polymer, in which polymers are usually dissolved in organic solvents to enhance the effectiveness of the amination reaction. Generally, aminated polymers become more hydrophilic, biocompatible, adhesive and selective, and they are widely used as ion-exchangers,[8,9] biomaterials,[10] coatings,[11] and membranes in electrochemical devices.[12–14]

Recently, to achieve better hydroxide conduction in alkaline fuel cells, a hydrothermal amination process has been developed by Wang and coworkers[15] by adopting hydrothermal synthesis, which is widely used in the synthesis of inorganic materials and nanomaterials. However, these were prepared in porous powders form and also were insoluble in any common solvents. Therefore, it was not suited to preparing anion exchange membrane through direct casting.

In this work, to prepare anion exchange membranes effectively, the amination reaction between chlorinated polypropylene (CPP) and ethylenediamine (EDA) was initiated with a mixture solution of a highly polar aprotic solvent (acetone) and a nonpolar solvent (toluene), and at controlled temperatures (≤55°C). New anion exchange membranes were prepared directly from aminated polymer solution, and then membrane properties, such as the structure, water uptake, ion exchange capacity (IEC), fixed ion concentration (FIC), ion conductivity, were examined.

EXPERIMENTAL

Amination and membrane casting

Two gram of chlorinated-polypropylene (CPP, $M_w =$ 150,000) was dissolved in 25 mL toluene in a flask, and 2 g of ethylenediamine (EDA, $M_w = 541.566$) was dissolved in 50 mL acetone in another flask.

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After two polymers were wholly dissolved, water contained in solution was removed with anhydride magnesium sulfate ($MgSO_4$). Two dissolved solutions were poured into a round-bottomed flask that contained a magnetic stirring bar, and then were mixed. All the reagents for the experiment were obtained from Sigma-Aldrich Co. and were of analytical grade. Also, these used without further purification.

To aminate, the mixed polymer solution was heated with water-bath at different temperatures (30, 40, 50, and 55°C) for 48 h. Inert gas (argon or nitrogen) was purged in the system during the entire experiment.

After the amination reaction, membranes were obtained by the casting of an aminated solution onto a clean glass plate, and were dried at room temperature for 24 h. Aminated membranes were peel off the glass plate and were washed repeatedly with deionized water. Finally, they were dried in an oven at 60°C for 24 h, then at 105°C overnight. Aminated membranes were denoted based on the names of the polymers and amine. So, Aminated membranes, which obtained by amination CPP and EDA, were referred to as CPP-EDA membranes.

Characterization

An FTIR spectrometer (Spectrum GX, Perkin–Elemer Co.) was used to record the spectrum. An average of 20 scans with a resolution of 1 cm^{-1} was recorded. The samples were prepared by a KBr wafer technique.

The cross-section and surface morphologies of membranes were observed with a scanning electron microscope (SEM; JEOL 6300F, JEOL). The membrane samples frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis.

Thermogravimetry analysis (TG) of the membrane sample was performed by a Pyris 1 thermogravimetric analyzer (TGA; Perkin–Elmer). All analyzes were conducted in an N_2 purge (40 mL/min) using sample weights 3–7 mg over a temperature range 30–700°C at heating rate of 5°C/min.

Membrane samples prepared for elemental analysis were dried in a vacuum oven at 60°C for 1 day. All analyzes were carried out by the Korea Testing and Research Institute (Seoul, Korea).

The degree of amination was calculated from the elemental analysis results using the following formulae:[16]

$$\text{Degree of amination (\%)} = \frac{C_1 - C_2}{C_1} \times 100$$

where C_1 and C_2 are the chlorine contents (mmol/g) of the CPP and the CPP-EDA membrane, respectively.

IEC of the CPP-EDA membranes was determined by Mohr method.[9,15] 0.5 g of the CPP-EDA membrane was treated in 1M HCl solution at room temperature for 5 h to ensure complete protonation and conversion into the chloride salt. After filtering, the membrane was repeatedly washed with deionized water. Then, to exchange chloride ion with hydroxide ion, the membrane in the chloride form was immersed 0.5 M NaOH solutions for 1 day. 10 mL of the chloride ion solution was taken and then neutralized with 1 M HNO$_3$ solution. The chloride ion content was determined by a titration of 0.1 M-AgNO$_3$ solution with K_2CrO_4 as an indicator. IECs were calculated from the released chloride ions and the mass of dried membrane (mmol/g).

Water uptake of membrane (W_M) was obtained by taking the wet weight (g) and dry weight (g) of the CPP-EDA membrane sample. To obtain the wet weight, the membrane sample was dried at 100 ± 5°C for 1 day and then was soaked in distilled water at room temperature for 1 day. The wet sample was then removed and was weighed immediately after blotting the free surface water. The dry weight and wet weight were measured in a capped weighting bottle. The W_M was expressed in g of H_2O /g of dry membrane.

The fixed ion concentrate (FIC), which is known as a factor related to the selectivity, can be calculated with the following formula:[4,17,18]

$$\text{FIC (mequiv/g } H_2O) = \frac{\text{IEC}}{W_M}$$

The ion conductivity (K) of the CPP-EDA membrane was measured with an impedance analyzer (μAutoLablll AFR2, Eco Chemie B.V). The impedance spectra were recorded in the frequency range from 10 kHz to 100 Hz with ac single amplitude of 10 mV and at room temperature. Before the experiments, the membrane was conditioned for 1 day in 0.1 M NaCl electrolyte solution. The ion conductivity was obtained using the following expression:[4,13,18]
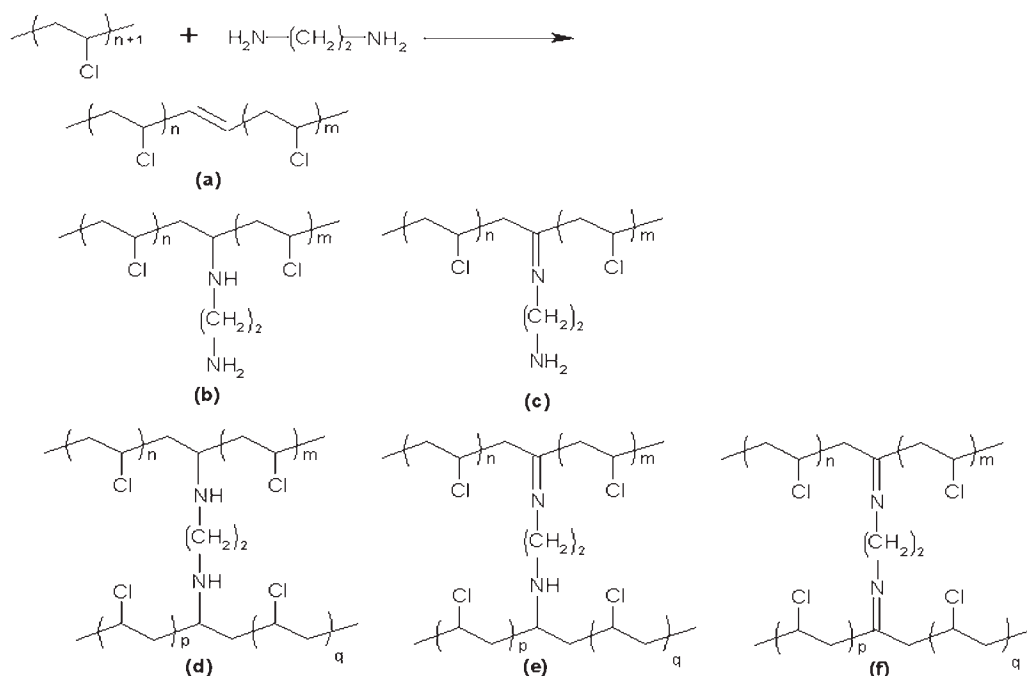
$$K = \frac{L}{(R_1 - R_2) \times S}$$

where K is the ion conductivity (S/cm), L is the thickness of the membrane (cm), S is the area of the membrane (cm^2), R_1 and R_2 are the cell alternating-current impedance (Ω) with and without membrane, respectively.

RESULTS AND DISCUSSION

Amination

Figure 1 is shown the change to the CPP back-bone after the amination of CPP with EDA. It is known that

Figure 1 Possible reaction of CPP and EDA; (a) elimination reaction, (b)–(f) substitution reaction. Note that only the changes to the CPP back-bone are shown.

the reaction involves both elimination and substitution.[19,20] The elimination raises the color change that appears with time at temperature from white to shades of yellow (the limit of solubility), orange, brown, and finally black. Likewise, the substitution raises, in addition to a change in solubility and nitrogen content, the potentiometric and adhesive properties change.

FTIR analysis

The FTIR spectra of the CPP and the CPP-EDA membrane sample were shown in Figure 2. In the FTIR spectrum of the CPP membrane sample, the absorption bands at 794–670 cm^{-1} arise from stretching vibrations of C—Cl bonds. The absorption bands at 3303–2782 cm^{-1} are assigned to the C—H stretching vibrations. The peaks at 1461 and 1383 cm^{-1} are attitude to bending of C—H and stretching of C—C bonds. The band at 978 cm^{-1} is ascribed to CH$_2$ vibration. After amination, the intensities of the band at 794–670 cm^{-1} evidently drop. Also, new absorption bands appear at 1111, 3409 and 1659 cm^{-1} is due to amination. In contrast to the standard spectra, the broad band at 3409 cm^{-1} is due to the symmetrical and asymmetrical stretching vibrations of NH and NH$_2$, whereas the peak at 1111 and 1659 cm^{-1} is due to vibration of C—N—H or C=N.

Structure of membrane

Figure 3 presents the cross-section and surface morphologies of the CPP and CPP-EDA membrane,

which were observed with SEM. When the chlorinated polymer was aminated with a diamine (EDA), rugged textures with pores were observed [Fig. 3(c,d)]. This presumably results from the incorporation of hydrophilic EDA chains into hydrophobic CPP structure, and partially cross-linked structures. Likewise, when the solubility of the CPP-EDA membrane was tested in various solvents (such as tetrahydrofuran, dimethylsulfoxide, dimethylformamide, chloroform, and toluene), and in common acid and base solution (such as HCl, H$_2$SO$_4$, and NaOH), the cross-linked membrane did not dissolved but merely swelled in these solvents.
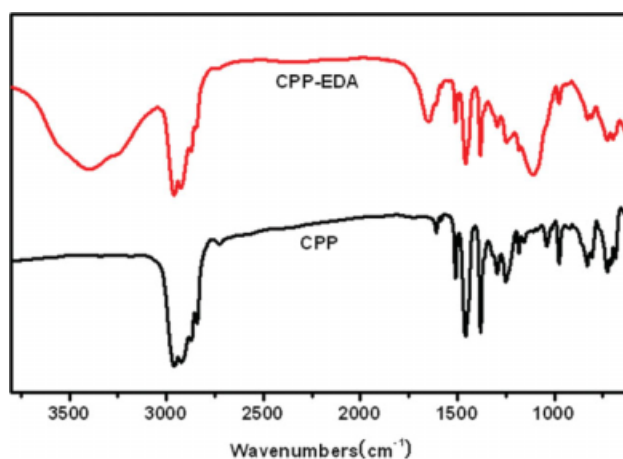
Figure 2 FTIR spectra of the CPP and CPP-EDA membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
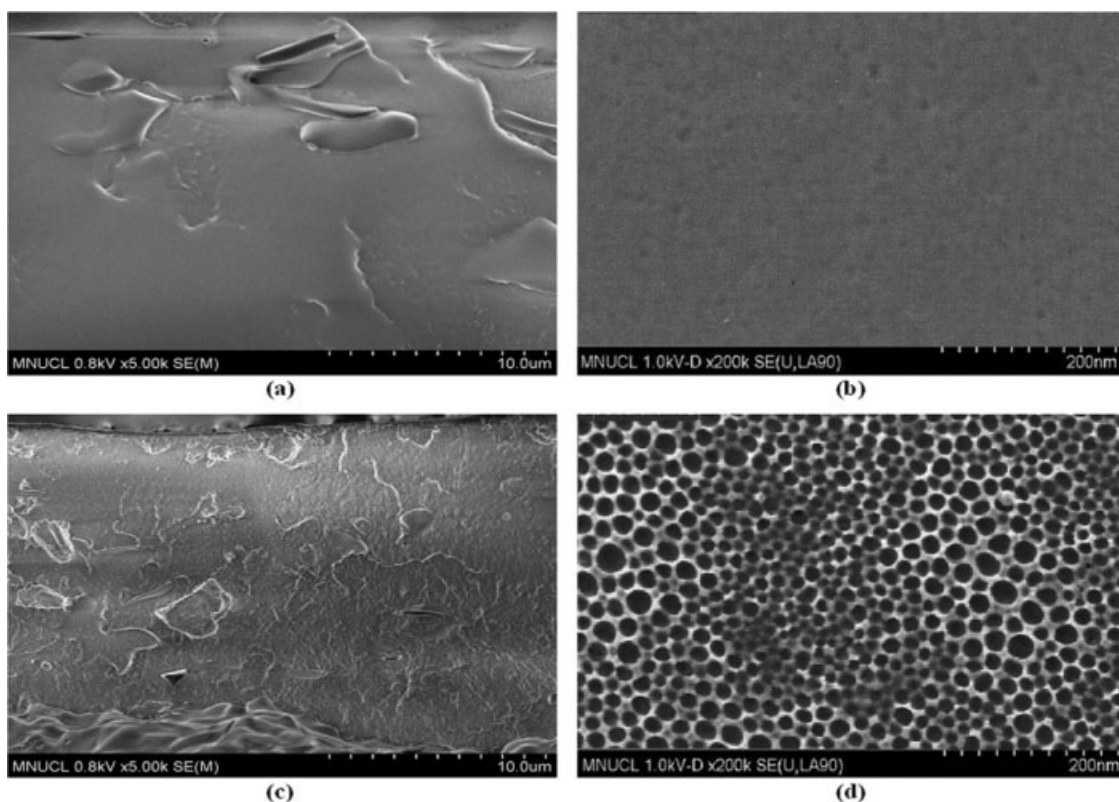
Figure 3 SEM images of cross-section of (a) CPP and (b) CPP-EDA membrane.

Thermogravimetry (TG)

Figure 4 shows the TG curves of the CPP and the CPP-EDA membrane prepared with CPP, and with CPP and EDA. The CPP-EDA membrane experiences more mass loss than CPP membrane. Moreover, at below 400°C, the CPP-EDA membrane was more the mass loss than the CPP membrane. It was likely due to decomposition and to deamination of the CPP-EDA membrane. These results imply that the decomposition of the CPP-EDA membrane was accelerated because its back-bone was attacked by the decomposed amine groups during deamination reaction.[4]

As the temperature reaches above around 450°C, the masses of both membranes tended to be stable. However, the CPP-EDA membrane produced more residues (carbon). During amination, EDA chains are randomly attached to CPP chain, and decomposition of partially cross-linked interpenetration structures lead to more residues.[21]

Elemental analysis

The elemental analysis and titration results for the CPP and CPP-EDA membrane at various temperatures for 48 h were summarized in Table I. The chlorine content of the CPP membrane was 9.18 mmol/

g, and those of the CPP-EDA membranes were 4.95, 4.86, 4.54, and 3.99 mmol/g at different temperatures (30, 40, 50, 55°C), respectively. Likewise, the CPP-EDA membranes had nitrogen contents ranging from 6.50 to 8.72 mmol/g. In addition to the amination reaction (substitution reaction), which gave rise to the anion exchange of the polymer membrane, the elimination reaction between Cl and its adjacent H causes additional Cl loss, which could be seen by a
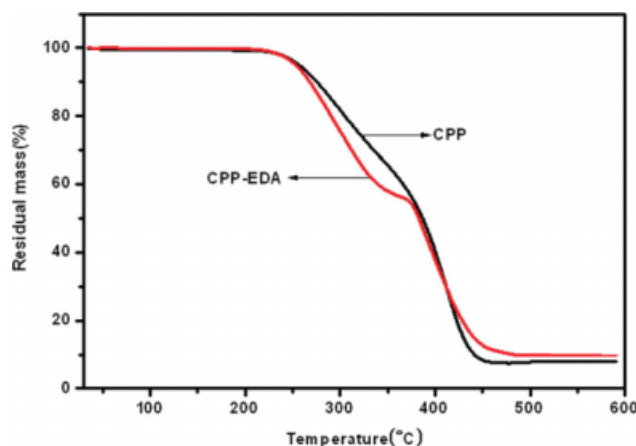

Figure 4 TG curves of the CPP and CPP-EDA membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Elemental Analysis and Titration Results

Element sample	C (%)	H (%)	O (%)	Cl (%)	Cl (mmol/g)	N (%)	N (mmol/g)
CPP	57.64	8.36	1.44	32.53	9.18	<0.3	–
CPP-DEA (30°C)	50.64	7.23	15.46	17.56	4.95	9.11	6.50
CPP-DEA (40°C)	50.08	8.43	14.96	17.22	4.86	9.31	6.65
CPP-DEA (50°C)	49.97	8.78	14.69	16.09	4.54	10.47	7.47
CPP-DEA (55°C)	51.41	9.22	13.03	14.13	3.99	12.21	8.72

comparison of the changes in the Cl content before and after amination and in the N content of the CPP-EDA membranes. Because of this elimination reaction, the polymer chains were cross-linked during the amination, as evidenced by the fact that the CPP-EDA membrane was insoluble in various solvents such as tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, chloroform, and toluene. By comparing the nitrogen contents obtained with elemental analysis and titration, it can be seen that the majority of functional groups, such as NH or NH_2, were accessible. It can be concluded that the chlorinated aliphatic polymer was successfully functionalized. Figure 4 shows the degree of amination of the CPP-EDA membranes aminated at different temperature. The degree of amination was 46.05, 47.07, 50.56 and 56.58% for CPP-EDA membrane aminated at 30, 40, 50, and 55°C, respectively.

Water uptake and ion conductivity

The ionic conductivities and water uptake of the CPP-EDA membranes are shown in Figure 5. These values were measured at room temperature. The water uptake of the CPP-EDA membrane increased with an increasing degree of amination. There was no water uptake in the CPP membrane, whereas the water uptakes of the CPP-EDA membrane were

0.153, 0.243, 0.309, and 0.410 g of H_2O/g of dry membrane, respectively, when the degrees of amination were 46.05, 47.07, 50.56, and 56.58%. As Figure 6 shows, increasing the degree of amination led to an increase in the water uptake. That is to say, the increasing water uptake implies that the chloride groups of the CPP membrane were substituted by many hydrophilic amine groups.

The CPP membrane showed an ionic conductivity of 5.75×10^{-7} S/cm at room temperature, whereas, as Figure 6 shows, the CPP-EDA membranes showed ionic conductivities of 0.475×10^{-2}, 0.625×10^{-2}, 0.689×10^{-2}, and 0.999×10^{-2} S/cm, respectively, when the degree of amination were 46.05, 47.07, 50.56, and 56.58%. Ionic conductivities were high when the water uptakes were high, as Figure 6 shows. This implies that amination affected the water uptake, and the water uptakes affect the selective permeation of the membrane. Therefore, when the water uptake was highest, the ionic conductivity of the CPP-EDA membrane also was highest, as it is known.[4,17]

IEC and FIC

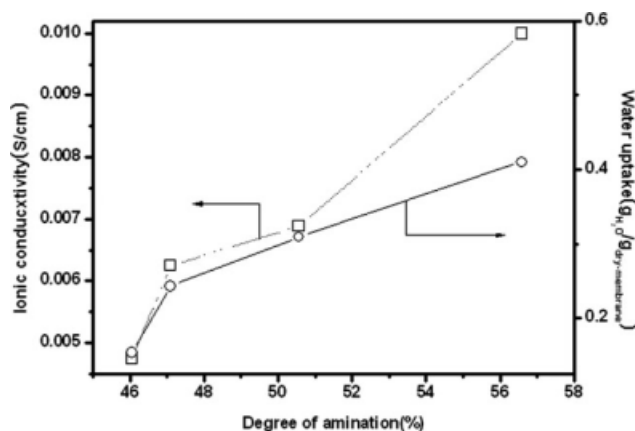Figure 7 illustrates the IEC and FIC and the degree of amination. With an increase in the degree of

Figure 5 Variations of the ionic conductivity and water uptake with the degree of amination.
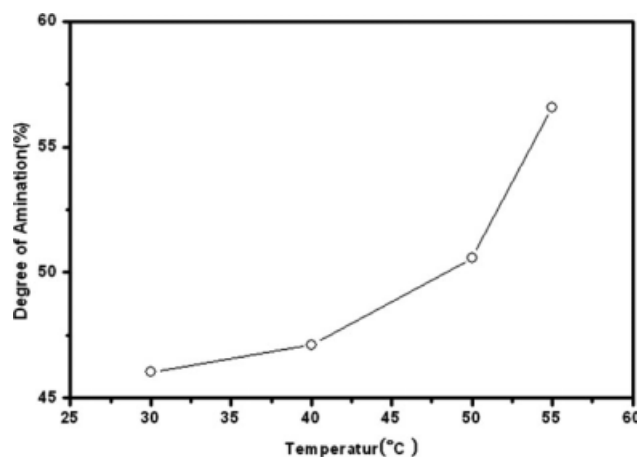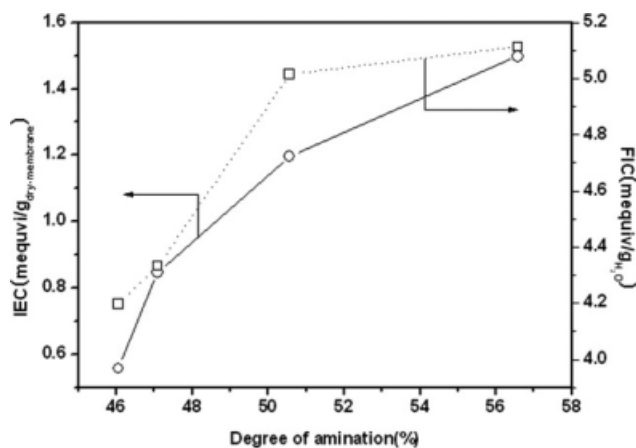

Figure 6 Degree of amination of membrane aminated at different temperatures.

Figure 7 Variation of IEC and FIC with the degree of amination.

amination, the IEC and FIC were increased. In general, increasing the FIC led to an increase in the IEC, as the results showed. From the data of the Figure 7, it seems that to obtain a higher IEC, the membrane should have a high FIC and a high degree of amination. The prepared membranes possessed IECs in the range of 0.557–1.498 mequiv/g of dry membrane and FICs in the range 4.198–5.114 mequiv/g of H_2O.

CONCLUSIONS

1. Anion-exchange membranes were prepared by the amination of CPP with EDA in a mixture of acetone and toluene at low temperature. The degrees of amination were 46.05, 47.07, 50.56, and 56.58% for the CPP-EDA membrane aminated at 30, 40, 50 and 55°C, respectively.
2. The CPP membrane had no water uptake, whereas the water uptakes of the CPP-EDA membrane were 0.153, 0.243, 0.309, and 0.410 g H_2O/g of dry membrane, respectively, at different aminated temperature. Also, The CPP-EDA

membrane possessed ionic conductivity in the range of 0.475×10^{-2}–0.999×10^{-2} S/cm.
3. The IEC and fixed ion concentrate of the CPP-EDA membrane increased as the degree of amination increased. The CPP-EDA membrane possessed IECs in the range of 0.557–1.498 mequiv/g of dry membrane and FICs in the range of 4.198–5.114 mequiv/g of H_2O.

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